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SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

Quarterly Summary Progress Report 2

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ABSTRACT

Three types of ligand-containing polymers that showed high stability to 40% KOH in our screening tests are now being comprehensively evaluated as battery separator materials. They are: 1) 2-vinylpyridine - methylmethacrylate copolymers, 2) styrene - maleic anhydride copolymers, and 3) polystyrenes containing ligand substituents. These polymers, either as unsupported films or as heterogenous membranes on polypropylene substrates, are being evaluated before and after a 60-hour exposure to 40% KOH saturated with silver oxides at 135°C. The properties measured in the study include dimensional stability, electrical resistance, electrolyte adsorption, tensile strength, pore size, and resistance to penetration by zinc dendrites. Membranes prepared from both 2-vinylpyridine - methacrylic acid and styrene - maleic anhydride have shown electrical resistances under 20 ohm-in. and survived the above exposure cycle satisfactorily

Polystyrenes with ligand substituents such as 8-hydroxyquinoline, 2-pyridylmethylamine, and iminodiacetic acid have also been prepared.

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I. INTRODUCTION

The primary objective of this program is the development of battery separator materials that will function satisfactorily in a sealed Ag-Zn secondary battery following heat sterilization at 135°C. Several types of ligand-containing vinyl polymers have been selected as candidates for this purpose. These polymers have the unique ability to restrict metal ion migration in the cell by chelation of these ions in the form of olated complexes.

Our program has been divided into the following four phases:

1. Preparation of model ligand-containing polymers.

2. Screening of the model polymers for thermal stability at 135°C and for hydrolytic stability in 40% KOH at 135°C.

3. Preparation of copolymers and membranes using polymer units that showed high stability in our screening test.

4. Comprehensive evaluation of our best membranes as battery separators.

In the first part of our program 28 polymers were screened for thermal stability and for stability in 40% KOH at 135°C. Three general types of polymers that showed high stability in these screening tests have been selected for comprehensive evaluation as separator materials. These polymers are:

1. 2-Vinylpyridine - methacrylic (and acrylic) acid polymers.

2. Polystyrenes with ligand substituents.

3. Styrene - maleic anhydride copolymer.

During this report period our specific objectives were to:

1. Start a comprehensive evaluation of the polymers that showed promise in the screening program.

2. Prepare ligand polymers derived from polystyrene, poly (vinylbenzyl chloride) and poly (vinylbenzyl chloride) - methyl methacrylate copolymer.

3. Continue to screen new candidate polymers for stability in 40% KOH at 135°C.

II. SUMMARY

A comprehensive evaluation of the following three types of polymers as battery separator materials was started:

1. 2-vinylpyridine - methyl methacrylate and methyl acrylate copolymers
2. Styrene - maleic anhydride copolymers
3. Polystyrenes with ligand substituents.

These polymers are being evaluated as unsupported films or as heterogenous membranes prepared by casting polymer in a porous polypropylene substrate. Stability and durability of these membranes at 135°C in 40% KOH and in 40% KOH saturated with silver oxides is determined by measuring the following properties of the membranes before and after exposure.

1. Dimensions
2. Electrolyte adsorption
3. Electrical resistance
4. Appearance
5. Tensile strength

In addition, tests to measure pore size and resistance to penetration by zinc dendrites have been initiated.

Durable 2-vinylpyridine - methacrylic acid films were made by the *in situ* saponification of 2-vinylpyridine - methyl methacrylate copolymers in 40% KOH. These membranes were more durable than 2-vinylpyridine - acrylic acid films prepared by a similar procedure, or the 2-vinylpyridine - methacrylic acid heterogenous membranes. Acid content in the range 55 to 65 mole-% in these saponified copolymers gave the films with the best combination of low electrical resistance and good durability in 40% KOH. Films of this type had approximately 7 ohms-in. resistivity in 40% KOH both before and after 60 hours exposure at 135°C in 40% KOH saturated with silver oxides, and wet (with 40% KOH) tensile strength after exposure up to 1000 psi. Similar, unsupported styrene - maleic anhydride copolymer films have shown lower electrical resistances and slightly better resistance to penetration by zinc dendrites than 2-vinylpyridine copolymer films. Other ligand polymers were also prepared by polymerizing maleic anhydride and diethyl fumarate with 2-vinylpyridine. However, both copolymers had low molecular weight and did not give usable films.

Ligands are also being substituted onto polystrene and polystrene - methyl methacrylate backbones. Polymers of these types that were prepared include poly(vinylbenzyl-2-pyridylmethylamine)-methyl methacrylate copolymer, poly[N-ar-vinylbenzyl) iminodiacetic acid], and poly[4,5-(methylene-8-hydroxyquinolino)vinylbenzene]-styrene copolymer.

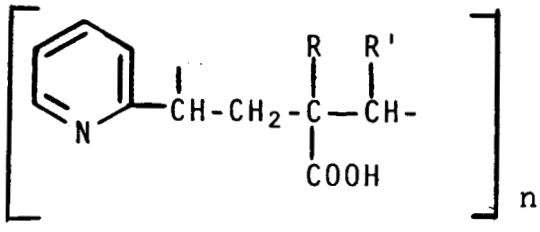
Poly(4,6-diamino-2-vinyl-*sym*-triazine) was also prepared. However, this polymer decomposed in 40% KOH at 135°C.

III. DISCUSSION OF RESULTS

A. SYNTHESIS OF LIGAND-CONTAINING POLYMERS

1. Vinylpyridine Copolymers

2-Vinylpyridine copolymers containing the ligand grouping shown below were found to be exceptionally stable in 40% KOH.



Although the first polymers of this type tested, 2-vinylpyridine-methacrylic acid copolymers, gave poor films, usable membranes were made by the *in situ* saponification in 40% KOH of a film of the corresponding ester copolymer (ref. 1).

Several types of 2-vinylpyridine copolymers, discussed below, were prepared to find polymer configurations with the optimum combination of film-forming ability and low electrical resistance. Data describing these polymers are in Table 1. They were prepared by bulk polymerization in a nitrogen atmosphere.

a. 2-Vinylpyridine-Methyl Methacrylate and Acrylate Copolymers

Copolymers with varying ester contents from which the corresponding acid copolymers are derived by *in situ* saponification in base were prepared. All the ester polymers yielded flexible films. Acid copolymers derived from the corresponding methacrylate ester copolymers retained shape and strength better than those derived from acrylate ester. All future optimization work is being done with the methacrylate copolymers.

b. 2-Vinylpyridine-Diethylfumarate Copolymer

The polymer prepared by copolymerization of a 1:1 charge of monomers had a 0.66:0.34 monomer composition. Its molecular weight, based on viscosity, was very low and the polymer gave very brittle films. No future work with this pair is planned.

Table 1

PROPERTIES OF COPOLYMERS

Ref.	Monomers*	Mole Ratio Monomers Charged	Reaction Time, hr at 60°C	Conversion wt-%	Solvent/Non-solvent used for Purification	Mole Ratio Monomers in Polymers**
94541	2-VP: methylacrylate	0.60:0.40	3	35	benzene/hexane; acetone/ hexane	0.75: 0.25
94540	2-VP: methylacrylate	0.33:0.67	3-1/2	32.5	benzene/hexane	0.56:0.44
94561	2-VP: methyl methacrylate	0.20:0.80	5	13	benzene/hexane	0.32:0.68
94562	2-VP: methyl methacrylate	0.10:0.90	4	12	benzene/hexane	0.23:0.77
94567	2-VP: methyl methacrylate	0.30:0.70	7	22	benzene/hexane	0.45:0.55
94528	2-VP: diethylfumurate	0.50:0.50	18	14	benzene/hexane	0.66:0.34
94507	2-VP: methacrylic acid: butylvinyl ether	0.15:0.30:0.55	51	8	benzene-methanol/ hexane	0.33:0.34: 0.33
94524	2-VP: methacrylic acid: butylvinyl ether	0.33:0.33:0.33	70	2.5	acetone/hexane	0.55:0.34: 0.11
94514	2-VP: maleic anhydride butylvinyl ether	0.33:0.33:0.33	4	--	acetone/hexane	0.25:0.64: 0.11
94525-1	2-VP: maleic anhydride butylvinyl ether	0.40:0.20:0.40	18	10	acetone/hexane	0.32:0.59: 0.09
94548	2-VP: maleic anhydride	0.67:0.33	4	6.7	-----/methanol; -----/hot benzene	0.16:0.84
94551	Vinylbenzylchloride: methyl methacrylate	0.50:0.50	33***	33	benzene/hexane	0.56:0.44
94577	Vinylbenzyl chloride: methyl methacrylate	0.50:0.50	43***	43	benzene/hexane	0.53:0.47

* 2-VP is 2-vinylpyridine

** Based on elemental analysis

*** 0.2% Azo-bis-isobutyronitrile

c. 2-Vinylpyridine-Methacrylic Acid-Butylvinyl Ether Terpolymers

A technique for improving the film-forming characteristic of methacrylic acid copolymers directly is to incorporate butylvinyl ether units into the polymer chain. Two terpolymers of 2-vinylpyridine, methacrylic acid and butylvinyl ether were prepared. A polymer having approximately equal mole ratios of the three monomers had improved film-forming characteristics but had a high electrical resistance (31 ohms-in^2). A terpolymer with lower butylvinyl ether content (0.35:0.55:0.10) did not give a usable film. Viscosity measurements of both these polymers indicate that their molecular weights are low.

d. 2-Vinylpyridine-Maleic Anhydride Polymers

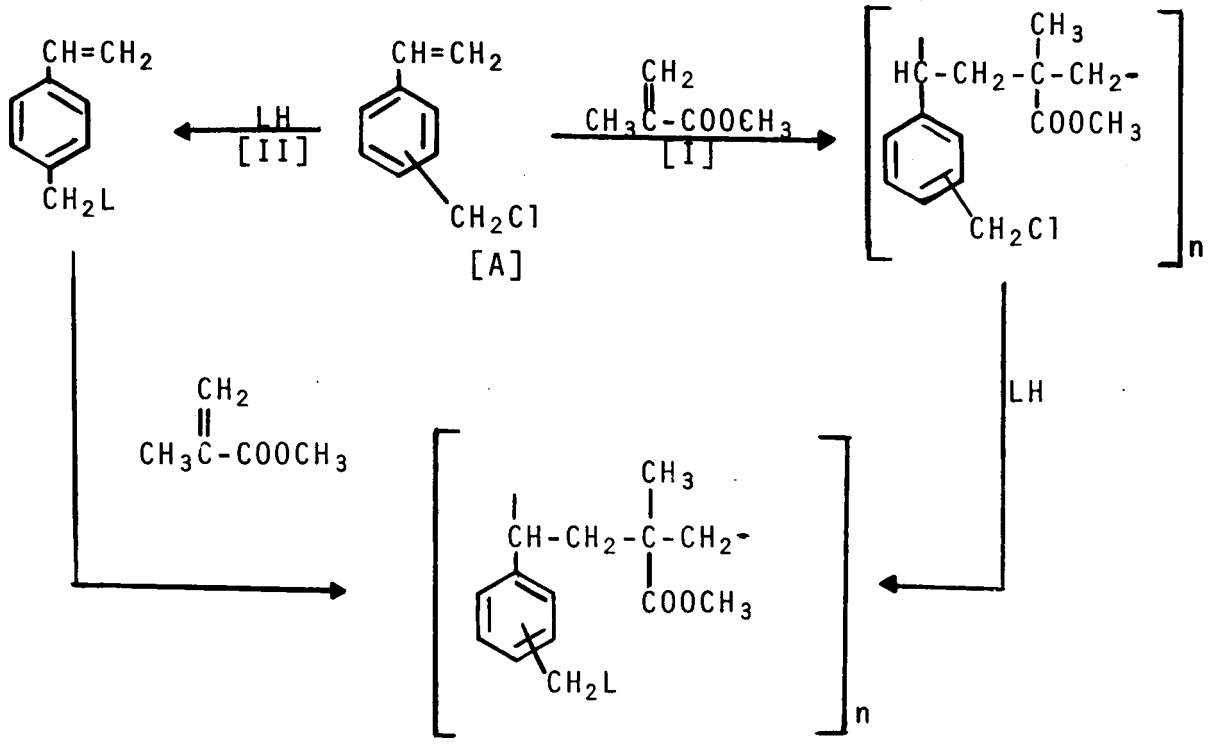
This type was chosen both because of its easy conversion to the free acid form and because it does not give any volatile products on hydrolysis. Several attempts were made to prepare 2-vinylpyridine-maleic anhydride-butylvinyl ether terpolymers and 2-vinylpyridine-maleic anhydride copolymers with both free radical catalysts and zinc chloride catalysts. All polymers were brown powders, and measurements of viscosity of solutions of two of the polymers indicated that they have low molecular weights. The maleic anhydride content of these polymers, especially the copolymer, are very high. These properties suggest that the products are low molecular weight complexes. No further work with this system is contemplated.

2. Substitution of Ligands on Styrene Polymers and Copolymers

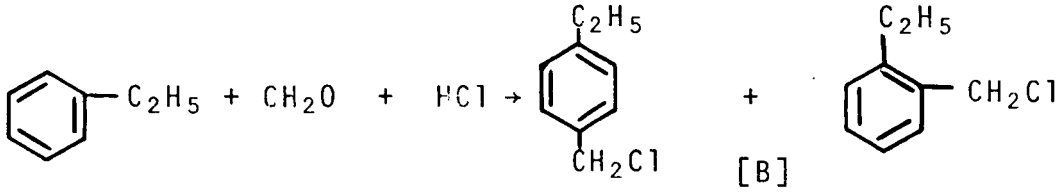
a. Copolymers

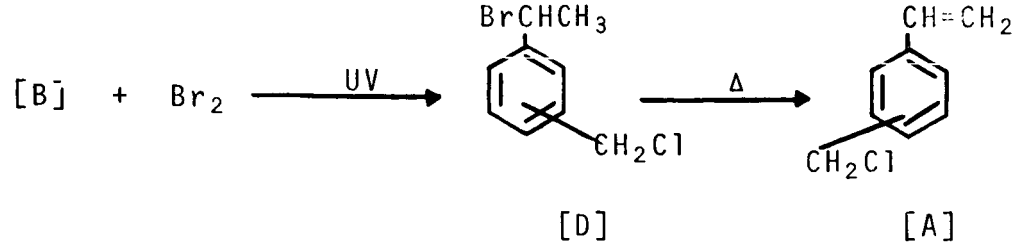
Techniques to substitute ligands onto copolymers such as polystyrene-methyl methacrylate are being developed so that the properties of these polymers can be tailored more closely to the requirements of the separator material. Methyl methacrylate was chosen as comonomer with styrene for three reasons. First, it copolymerizes well with styrene monomer; second, it increases the flexibility of the polymer; and third, it lowers the resistivity of the polymer after saponification.

Two routes, illustrated below, for preparation of these polymers are being used. In this scheme LH represents the ligand.

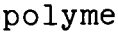


The starting reagent in this method, ar-chloromethylstyrene [A] was prepared using the procedure described by Clarke (ref. 2).





The product [A] consists of about 70% *para* isomer and 30% *ortho* isomer.

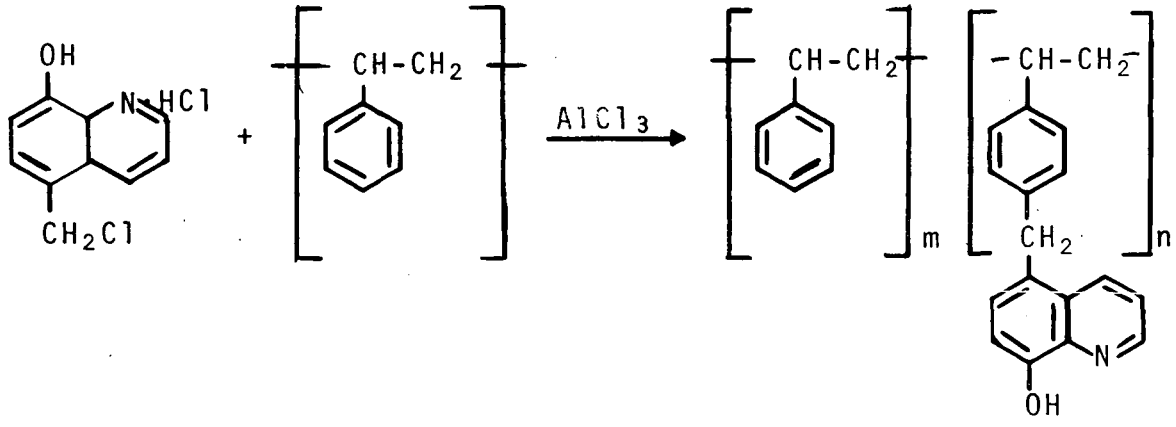
Poly(vinylbenzyl-2-pyridylmethylamine)-methyl methacrylate copolymer, where LH is  , was prepared by both routes. A higher molecular weight polymer (softening range 120-140°C, and relative viscosity of 1% solution, 1.15) was obtained by Route I. The rate of polymerization of vinylbenzyl-2-pyridylmethylamine with methyl methacrylate (Route II) was extremely low and the low molecular weight product isolated after 80 hours at 80°C had a softening range 75-100°C (relative viscosity of 1% solution, 1.05). The rate of homopolymerization of this monomer at 80°C was also low.

b. Iminodiacetic Acid Ligand on Polystyrene

The homopolymer, poly[N-(ar-vinylbenzyl)iminodiacetic acid] was prepared to determine the stability of the iminodiacetic acid group in 40% KOH. The polymer was prepared from its monomer by polymerization with persulfate catalyst in water. The monomer was prepared by reaction of the sodium salt of iminodiacetic acid with chloromethylvinylbenzene using a procedure described by Morris (ref 3).

c. Substitution of 8-Hydroxyquinoline on Polystyrene

We found that 8-hydroxyquinoline could be substituted onto polystyrene by the Friedel-Crafts reaction in nitrobenzene of polystyrene with 5-chloromethyl-8-hydroxyquinoline hydrochloride. In this preparation polystyrene with molecular weight 20,000 was used.



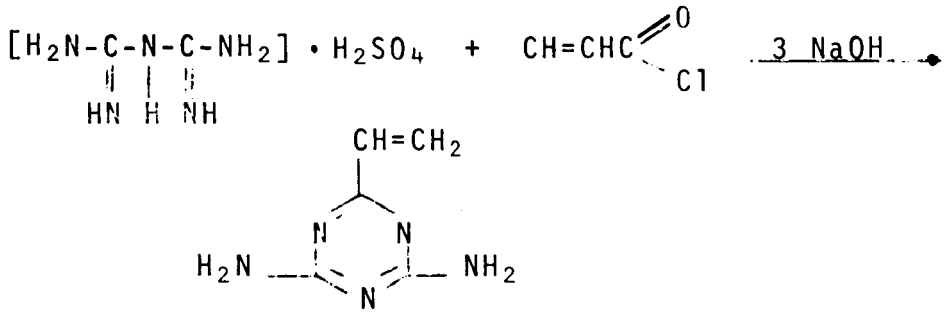
The product obtained using 0.5 mole of chloromethyl compound per styrene unit contained about 27% substitution and had a softening range of 123-145°C.

d. Ligand Substituents on High Molecular Weight Polystyrene

New preparations of poly(vinylbenzylcatechol) and poly(vinylbenzyl-2-pyridylmethylamine) from polystyrene with molecular weights of about 100,000 were also made using the same procedure as before (ref. 1) except that the polymers were retained in solution. The polymers were not isolated since we found that the polymers prepared previously would not redissolve after solvent had once been completely removed. The solutions of polymers were used to cast films. However, the films prepared (alone or on polypropylene substrate) were brittle and not usable.

3. Polymers from 4,6-Diamino-2-Vinyl-*s*-Triazine

4,6-Diamino-2-vinyl-*sym*-triazine was prepared by reaction of biguanide sulfate with acrylyl chloride in basic medium (ref. 4).



The monomer polymerizes readily in aqueous solution with persulfate catalysis. An attempt to copolymerize this monomer with methyl methacrylate was unsuccessful.

4. 2-Vinyl-6-Aminopyridine

Two further attempts to prepare 2-ethanol-6-aminopyridine, the intermediate for proparation of the above monomer, using the general procedure described by Cislak (ref. 5) were made. In one, xylene was used as solvent for reaction of sodamide with 2-ethanolpyridine; in the other, dimethylaniline was used as solvent. None of the desired product was isolated in either attempt.

B. SCREENING TESTS FOR POLYMER STABILITY

1. Thermal Stability at 135°C

Results of isothermal gravimetric analysis of polymers tested are shown in Table 2. The method of analysis was the same as that described in the first quarterly report (ref. 1). Two terpolymers containing methacrylic acid groups in the chain dehydrated partially under these conditions as evidenced by a decrease in acid functionality and appearance of anhydride groups in the infrared spectrum. This type of dehydration was detected previously in other copolymers containing carboxylic acid groups. Changes in other polymers tested were minor.

2. Hydrolytic Stability in 40% KOH at 135°C

The test procedure used to measure stability of polymers in 40% KOH at 135°C was described before (ref. 1). Results of tests done in this report period are listed in Table 3.

Total recovery of 2-vinylpyridine-methyl methacrylate polymers was over 90% with the exception of the polymer with high acid content (77%) that dissolved on hydrolysis (120-hr exposure). The other polymers were only partially saponified during the 60 hr exposure period. The recovered polymers were isolated in two fractions. The saponified fraction was soluble in dilute caustic. Its spectrum in the acid form was identical to that of a sample of polymer saponified in alcoholic 1N NaOH. The spectrum of the potassium salt of this fraction showed no residual ester functionality. The spectrum of the water-insoluble fraction was identical to that of the original ester form of polymer. The percentage recovered in the ester form was 72% for the 0.54:0.46 polymer (94503) and 51% for the 0.38:0.62 polymer (94505). A similar 2-vinylpyridine-methyl acrylate copolymer is saponified completely in these conditions.

Weight losses of the 2-vinylpyridine-methacrylic acid-butylvinyl ether terpolymers were higher than would be expected. No changes in chemical structure of recovered polymers were detected and it appears that this weight loss is due to solubility of low molecular weight fractions in 40% KOH.

Polyacrylonitrile dissolved completely under test conditions, illustrating the large difference in stability of the homopolymer compared to styrene-acrylonitrile copolymer that hydrolyzed only slightly under the same conditions (ref. 1).

Table 2

THERMAL STABILITY OF MODEL POLYMERS AT 135°C IN NITROGEN ATMOSPHERE

Ref/Source	Polymer	Weight Loss, % 24 hr.	Weight Loss, % (X) hr.	Change in IR Spectrum After Exposure	Change in Appearance After Exposure
94503	2-Vinylpyridine-methyl methyacrylate copolymer	8.5	8.5(70)	none	v. slight yellowing
94509	2-Vinylpyridine-meth-acrylic acid-butylvinyl ether terpolymer	15.5	17.3(71)	5.55, 5.70μ new; 9.55, 11.0μ dec.	none
94507	2-Vinylpyridine-methyl-acrylic acid-butylvinyl ether terpolymer	9.0	ca.25*(71)	5.55, 5.70μ new; 5.75, 11.0, 12.0μ dec.	fused, porous from gas evolution
94528	2-Vinylpyridine-diethyl fumurate copolymer	5.8	5.1(48)	general broadening 5.80μ decrease	fused and black
94533	Poly(2-vinyl-4, 6-diamino-triazine)	1.4	0.5(65)	none	none
CN 54	Styrene-acrylonitrile copolymer	0.53	0.76(66)	none	none
97004	Poly[4-5(methylene-8-hydroxyquinolino) vinylbenzene]-styrene	0	1.4(66)	3.0, 6.5μ decrease	sintered
94554	Polyvinylbenzylchloride-methyl methacrylate	0.3	2.0(120)	5.65μ new; general broadening	
	Poly[N-(ar-vinylbenzyl) iminodiacetic acid]	2.5	5.6(60)		

*mechanical loss of sample by overflow from sample crucible during gas evolution.

Table 3

STABILITY OF CANDIDATE POLYMERS AT 135°C IN 40% KOH

Source/Ref	Polymer	Wt.Loss, % after 63 hr.	Change in Appearance	Change in IR Spectrum	Viscosity Comparison		Softening Point, °C	
					n before	n after	Before	After
94503	2-Vinylpyridine-methyl methacrylate (0.54:0.46)	10.0	light brown	none(E) none(A)	1.56(E) 1.39(A)	1.53(E)	125-230(E) 220-265(A)	125-225(E)
94505	2-Vinylpyridine-methyl methacrylate (0.38:0.62)	8.7	light brown	none(E)	1.67(E)	1.72(E)	115-240(E)	110-245(E)
94507	2-Vinylpyridine-methacrylic acid-butylvinyl ether terpolymer	25.1	darkened	dec. 9.8, 11.0μ	1.08	1.13	95-150	
94509	2-Vinylpyridine-methacrylic acid-butylvinyl ether terpolymer	11.1	black	sl.dec. 11.0μ	1.08	1.08	190-240	225-245
94533	Poly(2-vinyl-4,6-diamino-s-triazine)	Sample dissolved						
94562	2-Vinylpyridine-methyl methacrylate (0.23:0.77)	Sample dissolved in 120 hr. test						
Acrilan®	Polyacrylonitrile	Sample dissolved						

C. COMPREHENSIVE EVALUATION OF LIGAND POLYMERS AS BATTERY SEPARATOR MATERIALS

1. General

Film samples of polymers are being tested for stability and durability in 40% KOH and in 40% KOH saturated with silver oxides at 135°C. The following properties of the films are being measured before and after exposure.

1) Dimensions

2) Electrolyte adsorption

3) Electrical resistance

4) Appearance

5) Tensile strength

In addition, tests to measure pore size and resistance of separator materials to penetration by zinc dendrites have been started. These properties were measured following general procedures developed for evaluation of separators for silver-zinc batteries (ref. 6) as follows.

a. Electrical Resistance

This test method was described in our first report (ref. 1).

b. Tensile Strength

(See Section 6)

c. Pore Size

Straight through pore sizes are measured by the electrolyte permeability method of Salkind and Kelley (ref 6).using 40% KOH electrolyte. Constants for 40% KOH used in the calculation of pore radius were 1.396 g/cc density and 0.033 g/cm-sec viscosity.

Data obtained by measuring adsorbance of electrolyte, pore size, electrical resistance, and dimensional changes after soaking in electrolyte were used to calculate effective porosity and to estimate the tortuosity of the pores. The tortuosity factor was calculated by the equation (ref. 7):

$$TF = \sqrt{\frac{\rho_{membrane}}{\rho_{KOH}} \text{ (Effective Porosity)}}$$

Results of initial tests are listed in Table 6.

d. Zinc Penetration Test

A test procedure similar to that described by Dalin and Solomon (ref. 6) was used. The test cell is identical to theirs. Current (10 ma) is supplied by an Acopian Model K-55 power supply with a rheostat and metered by a Weston Model 911 d-c milliammeter. Traversal is the time required for the voltage to drop below 1 volt. This time is measured by conveying the reference voltage from a Hewlett-Packard Model 412A d-c vacuum tube voltmeter to a Simpson meter relay that activates an Eagle signal timer at this shut-off voltage.

The separators are presoaked for at least 16 hours in the test solution, 1M ZnO in 40% KOH.

2. 2-Vinylpyridine-(meth)acrylic Acid Copolymers

Initial tests to measure the stability of the membranes at 135°C in 40% KOH saturated with silver oxides have shown that the polymers are stable in this environment. Our efforts are now directed at finding the optimum composition of copolymer and improved methods of membrane preparation, including saponification conditions for the ester precursors, for making a durable membrane with low electrical resistance. Results of evaluation tests are summarized in Tables 4, 5, and 6.

Both 2-vinylpyridine-methyl acrylate and 2-vinylpyridine-methyl methacrylate copolymers form excellent films. Several saponification conditions were tried with these polymers to determine the best way of preparing the free acid groups while retaining film integrity. The methacrylate polymers are more resistant to saponification and require longer reaction times under all conditions. The best medium found so far is 40% KOH at 135°C. Other hydrolysis media that were tried, but found either ineffective within reasonable reaction times and/or dissolved the resultant polymer are listed below:

1. 1N HCl saturated with NaCl

2. 1N NaOH

Table 4

PROPERTIES OF SEPARATOR MATERIALS IN 40% KOH

		Original Properties After Soaking Overnight In 40% KOH						Properties After 63 Hr. at 135°C in 40% KOH					
Ref.	Polymer	Dry Thickness (mils)	Thickness (mils)	Wt. Gain (%)	Area Retention (%)	AR (ohm-in.^{2})	ρ(ohm-in.)	Thickness (mils)	Wt. Gain (%)*	Retention (%)*	AR (ohm-in.^{2})	ρ(ohm-in.)	Comments
89794	2-VP-methacrylic acid (0.54:0.46) on polypropylene	5.3 ± 0.3	5.98 ±0.3	51.6	100	0.375	65.4	12.7 ± 1.6	159		0.080	6.3	Some mechanical loss of sample
89795	2-VP-methacrylic acid (0.78:0.22) on polypropylene	8.99 ± 1.2	8.9	25.7	100	0.409	45.7	16.9 ± 1	302		1.79	106	Some mechanical loss of sample
94505	2-VP-methyl methacrylate (0.38:0.62)	1.8 ± 0.1 2.1 ± 0.2 1.9 ± 0.2			After exposure time 134 hours After exposure time 63 hours After exposure time 39 hours			7.3 ± 1 5.0 ± 1 2.6 ± 0.3	155 87 45	85 85 96	0.052 0.65 ± 2.8 to 3.6	7.1 130	
94505	2-Vinylpyridine-methyl methacrylate (0.38:0.62)				After exposure time 120 hours			10.6	---	97.3	0.046	4.36	
94667	2-Vinylpyridine-methyl methacrylate (0.45:0.55) on 4 mil polypropylene substrate	5.8			After exposure time 120 hours								
Lytron® 810	Styrene-maleic anhydride copolymer in polypropylene wrapper	3.95 ± 0.7	5.9 ± 0.2	134	100			21.3 ± 1.5 (includes wrapper)			0.545	25.6	
89999	Poly(2-vinyl-4,6-diamino-s-triazine) on polypropylene	10 ± 1	8 to 19	58.2	90	0.212	23.6**						
97004	Styrene-4-(methylene-8-hydroxyquinolino) vinylbenzene copolymer on polypropylene	4.6 ± 0.4	4.6 ± 0.4	25.4	100	2.75	595						

* From original dry weight
** Measured in 9 mil area

Table 5

STABILITY OF SEPARATOR MATERIALS IN 40% KOH SATURATED WITH SILVER OXIDES

Ref. No./ Source	Polymer	Dry Thickness (mils)	Pre-Exposure	Properties After Pretreatment: Thickness mils	Wt. Gain, %	Area Retention, %	AR (ohm-in.^{2})	ρ ohm-in.	Properties After Exposure to 40% KOH Sat. with Silver Oxides For 63 Hrs.: Thickness, mils	Wt. Gain. % (From Dry)	Area Retention, %	AR (ohm-in.^{2})	ρ ohm-in.
Lytron® 810	Styrene-maleic anhydride between two 4 mil polypropylene sheets	3.4 + sheets 3.0 + sheets	135° -63 hr r.t.*	16.5	197	100	0.910	55	11.5	173	100	1.03	89
Lytron® 810	Styrene-maleic anhydride in polypropylene wrapper	(19.9)	none						23 ± 0.2	180	100	0.64	24.9
Lytron® 810	Styrene-maleic anhydride on polypropylene substrate	15.0 Same sample	r.t. 135° -63 hr	14.7 12.6	138 223	103 96	0.141 0.234	9.62 18.6	16.0		92.5	0.114	7.1
94541	2-Vinylpyridine-methyl acrylate (0.75:0.25) copolymer between 4 mil polypropylene		135° -63 hr none	12.1	---	100	9.94	822	11.2	---	100	5.19	464
89795	2-VP-methacrylic acid (0.78:0.22) conolymer on polypropylene	15.1 ± 1	r.t.	15.2	34.7	100	0.677*	46.7	23 ± 0.1	82		1.45	63
94505	2-VP-methyl methacrylate (0.38:0.62) polymer	1.8 ± 0.1 2.1 ± 0.2 1.7 ± 0.1	135°-134 hr 135°-63 hr none	7.3 ± 1 5.0 ± 1	155 87		0.052 0.65	7.1 130	6.1± 0.9 wrinkled 5 ± 1.2	156 174 70.5	100 --- 71	0.047 0.057 3.3 to 18	7.7 --- ---
94503	2-Vinylpyridine-methyl methacrylate (0.54:0.46)	2.3	135° 120 hr	11.5	155	99	0.888	77.3	7.2	140	99	1.105	154

* r.t. denotes samples that were soaked overnight in 40% KOH at room temperature; 135° denotes samples that were exposed to 40% KOH at 135°C for designated time.

Table E

ELECTRICAL RESISTIVITY, PORE SIZE AND RESISTANCE TO ZINC PENETRATION OF SEPARATOR MATERIALS

Sample No.	Polymer	History of Sample	Dry Thickness (mils)	Ratio Change Thickness to Wet Thickness	Specific Resistance (ohm-in)	Porosity from Electrolyte Absorption (1)	Effective Porosity from Conductivity (2)	Straight-Through Pore Size, μ	Tortuosity Factor (3)	Corrected Pore Size, μ (4)	Zinc Penetration Factor (5)
Chemstrand	Acrilan®, 3 oz/yd	Soaked overnight in test solution	7.3	0	3.1	0.302	0.283	1.0	1.03	1.03	~12
Lytron® 810	Styrene-maleic anhydride	"	6.4	0.33	10.1	0.513	0.0872	0.012	2.43	0.029	33,44(5)[6]
Gelvatol® 1-90	Poly(vinyl alcohol)	"	13	0.167	4.74	0.296	0.185	0.010	1.26	0.013	24 (2)[6]
89795	2-Vinylpyridine-methacrylic acid on polypropylene (0.78:0.22)	"	6.8	0	113	0.083	0.00778	0.93	1.03	0.96	10 (2)[6]
94567	2-Vinylpyridine-methyl methacrylate (0.45:0.55) on polypropylene	Heated at 135°C for 120 hr. in 40% KOH	5.8	0.23	12.7	0.485	0.0692	1.89	2.64	5.0	14 (2)[6]
94503	2-Vinylpyridine-methyl methacrylate (0.54:0.46)	Heated at 135°C for 120 hr. in 40% KOH and 63 hr. in 40% KOH sat. with silver oxides	2.3	0.68	153	0.325	0.0057	0.045	7.5	0.34	17 (1)[6]
94505	2-Vinylpyridine-methyl methacrylate (0.38:0.62)	Heated at 135°C for 134 hr. in 40% KOH and for 63 hr. in 40% KOH saturated with silver oxides	1.8	0.71	7.7	0.402	0.114	0.21	1.87	0.39	~12

Footnotes:

1) Pore volume from electrolyte absorption ÷ Wet volume of Separator

2) Resistivity of 40% KOH (ohm-in) ÷ Resistivity of Separator in 40 KOH = 0.879 ÷ separator in ohm-in

3) $\sqrt{\frac{\rho_{membrane}}{\rho_{KOH}}}$ (Effective Porosity)

4) Tortuosity factor x straight-through pore radius

5) Ave. Time To Traversal (min) ÷ Sample wet thickness (mils)

6) No. of samples tested for zinc penetration

3. 1N alcoholic NaOH saturated with NaCl

We have also found it necessary to support these films during hydrolysis in order to maintain reasonable film shape. The following methods of supporting these films have been tried: (1) holding the films between two pieces of silver screen, (2) clamping the film in a Teflon frame, (3) fastening the film on a Teflon cylinder with silver wire, and (4) casting film on polypropylene substrate and saponifying the resulting membrane without additional support.

Small samples have been successfully saponified to films with acceptably low electrical resistance by all the above methods, but the use of the cylinder support and use of polypropylene substrate have given films with fewer mechanical irregularities.

Membranes were also prepared by casting 2-vinylpyridine-methacrylic acid copolymers in polypropylene substrate. These films were flexible, but some polymer was mechanically lost from the substrate during exposure periods. The polymers used on these membranes were prepared directly by copolymerization of 2-vinylpyridine with methacrylic acid and have lower molecular weights than copolymers derived from hydrolysis of ester copolymers.

Results of our initial tests lead to the following conclusions.

1) Membranes derived from 2VP-methyl methacrylate retain shape better on saponification and have higher strength than those derived from 2VP-methyl acrylate.

2) Optimum acid concentration in linear copolymers is 55 to 65%. Membranes with acid contents under 50% have higher initial electrical resistances and larger increases in resistance after exposure to 40% KOH saturated with silver oxides. Initial tests of membranes that contain over 50% acid in the copolymer indicated that electrical resistance remains low after exposure to the silver oxides. We found that linear copolymers with acid contents over about 70% are not usable because of their high solubility in 40% KOH at 135°C.

3) Straight-through pore sizes were largest for supported (polypropylene substrate) films made either directly from an acid copolymer (89795) or by saponification of an ester copolymer (94567). The substrate also did not appear to improve resistance to zinc penetration.

4) Exposure of copolymer membranes to silver ions generally appears to increase electrical resistance and pore tortuosity. A few membranes for which we do not have pore size measurements have lower electrical resistance after exposure to silver ions.

3. Styrene-Maleic Anhydride

Two types of styrene-maleic anhydride membranes have been tested. The first are polymer films that are encased in polypropylene wrappers and pressed inside a silver screen. The second are copolymer films cast on a 4-mil polypropylene substrate. Electrical resistances for these composite membranes are acceptably low and remain low after exposure at 135°C to 40% KOH alone or saturated with silver oxides (Tables 4 and 5). The sample of polymer on the polypropylene substrate had the lowest resistance (9.6 ohm-in.), as would be expected.

Measurements of the resistance to penetration by zinc dendrites of unsupported styrene-maleic anhydride membranes indicate that it resists zinc penetration better than the vinylpyridine copolymers and polyvinylalcohol (Table 6).

4. Polystyrenes with Ligand Substituents

A membrane of the 4-(5-methylene-8-hydroxyquinolino)vinylbenzene-styrene 0.27:0.73 copolymer was prepared by casting a 20% solution of polymer in benzene onto a 3-mil polypropylene substrate. This membrane had high electrical resistance (2.75 ohm-in.^{2}). Our test results indicate that a higher degree of substitution of ligand in this type of polymer is needed to both lower resistance and raise the softening point of the polymer to a usable range for this program.

5. Poly(2-vinyl-4,6-diamino-*s*-triazine

Usable films of this polymer were prepared by casting a solution containing 20 weight-% polymer in 10% aqueous HCl on porous 3-mil polypropylene substrate. A sample of this film gained 58% in weight after soaking overnight in 40% KOH and had a resistance of 60 ohm-cm. This indicates that amino substituents may be as effective as carboxylic acid and hydroxyl groups in lowering resistivity of organic polymers. However, this particular polymer is not stable in 40% KOH at 135°C. A sample of the polymer in powder form hydrolyzed and evolved ammonia during the 60-hour screening test.

6. Tensile Strength of Membranes

Initial determinations of tensile strength of the most promising polymers were made. Tensile specimens were prepared by stamping out 1 x 5 in samples of our polymer films with a steel rule die. These specimens were tested in an Instron-Tensile Tester equipped with one inch "T" grips having sandpaper liner. The grip separation was 2.75 $\pm$0.25 in. and the crosshead speed was 0.5 in./min unless noted otherwise. Data are summarized in Table 7.

Tensile strengths of all the polymers tested in the dry form were acceptable. Reproducibility of the measurements of the styrene-maleic anhydride polymer was poor since it was difficult to obtain specimens free of all irregularities at the edges. Maximum strength obtained for this polymer in the dry condition was 2610 psi. In contrast, this polymer becomes extremely flexible after soaking in 40% KOH and elongations at break were 55 to 115% (315% at crosshead speed of 0.5 in./min).

The 2-vinylpyridine-ester copolymers have higher strengths and greater flexibility when dry. Initial tests indicate that sufficient strength is also maintained after saponification of this type of polymer in 40% KOH followed by exposure at 135°C to 40% KOH saturated with silver oxides. The samples tested were exposed in silver screen holders and contained some wrinkles. It is expected that higher mechanical strength will be obtained by improving methods of saponification of these films.

Table 7

TENSILE STRENGTH OF MEMBRANES AT ROOM TEMPERATURE

Polymer	Film Condition	No. of Specimens	Average Tensile Strength, psi
2-Vinylpyridine: methyl acrylate copolymer (0.56:0.44)	Dry	4	5800
2-Vinylpyridine: methyl methacrylate (0.38:0.62)	Dry	1	5030
2:1 Mixture of 2-VP: methylmethacrylate and 2 VP: methacrylic acid copolymers	Dry	3	2140
Styrene-maleic anhydride copolymer (1:1)	Dry	4	1760
Styrene-maleic anhydride copolymer (1:1)	Wet with water	1	940
Styrene-maleic anhydride copolymer (1:1)	Wet with 40% KOH	8	220*
2-Vinylpyridine:methyl methacrylate (0.54:0.46)	Wet with 40% KOH	1	1000
	after pre-exposure at 135°C for 120 hr to 40% KOH and 63 hr to 40% KOH saturated with silver oxides	1	388**
Styrene-maleic anhydride in 4 mil polypropylene wrapper	same as above	2	1370

*Crosshead speed 5 in/min; elongation at break 55 to 115%
**Visible nicks in sample

IV. PROGRAM PLAN

A. GENERAL

Our general approach can be divided into the following four phases:

1. Preparation of ligand-containing polymers.

2. Screening tests.

3. Preparation of copolymers and membranes.

4. Comprehensive tests.

Our program planning chart, showing the proposed distribution of effort to be expended on each of the phases, is given in Table 8.

B. ANTICIPATED WORK FOR NEXT QUARTER

1. Continue comprehensive evaluation of polymers that showed promise in the screening program as separator materials.

2. Substitute the ligands 8-hydroxyquinoline and catechol on a polystyrene-methyl methacrylate copolymer backbone.

3. Optimize mechanical characteristics of membranes made from 2-vinylpyridine-methyl methacrylate copolymers and styrene-maleic anhydride copolymers.

Table 8

OVERALL PROGRAM PLANNING CHART

Program Phase	Per cent of Total Research Effort									
	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb
1. Preparation of ligand containing polymers	80	80	80	40	20	20	20	--	--	--
2. Screening tests	20	20	20	20	10	10	10	10	10	
3. Preparation of co-polymers and membranes				40	40	40	40	50	60	10
4. Comprehensive tests					30	30	30	40	30	50
5. Final report										40

V. REFERENCES

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